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A New Mechanism for Hydrogen Desorption from Covalent Surfaces:
The Monohydride Phase on Si(100)

by

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Abstract

A new mechanism for the thermal desorption of molecular hydrogen from the monohydride phase on Si(100) has been identified. The unusual first-order desorption kinetics that are observed are due to the irreversible excitation of a hydrogen adatom into a delocalized, two-dimensional band state on the surface with an activation energy of 47 kcal/mol. The desorption reaction occurs between this excited hydrogen adatom and a second, localized hydrogen adatom. The mechanism was verified by adsorption of atomic hydrogen into the band state and the observation of reaction with localized deuterium adatoms at a temperature below that at which desorption from the surface normally occurs.

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In this Letter, we examine the isothermal recombinative desorption of hydrogen from Si(100) and identify a new mechanism for the desorption reaction. On metal surfaces, recombinative desorption proceeds via migration of adatoms from site to site until two adatoms in adjacent sites ultimately recombine and desorb. We shall show that this mechanism is inconsistent with the isothermal desorption kinetics of hydrogen from Si(100), measured between 685 and 740 K. We propose and verify that hydrogen adatom recombination from the surface of this covalent solid occurs via the irreversible excitation of an adatom to a delocalized, two-dimensional band state, followed by reaction of this delocalized adatom with a second localized hydrogen adatom to form a hydrogen molecule that desorbs.

Most investigations of the mechanisms of heterogeneous reactions involve studies on well-defined surfaces of metal single crystals. Only recently, have reactions been studied in comparable detail on surfaces of covalent solids. Silicon surfaces are currently being investigated intensively in this regard [1-3]. The Si(100) surface is particularly appropriate for such studies because the stable, reconstructed (2x1) structure is rather well characterized. In the absence of reconstruction, the silicon atoms would form a (1x1) surface structure characteristic of the bulk lattice, and each surface silicon atom would have two "dangling" bonds. On the reconstructed surface, silicon atoms in adjacent rows "pair up" to form a (2x1) array of dimers, resulting in only one dangling bond on each surface silicon atom [4]. In the monohydride phase of hydrogen on Si(100), there is one hydrogen atom bonded to each surface silicon atom resulting in the saturation of each dangling bond at the surface and the preservation of the (2x1)

reconstruction [5]. At higher coverages, some of the Si-Si dimer bonds are cleaved to form a dihydride phase in which, at saturation coverage, one-third of the surface silicon atoms are bonded to two hydrogen atoms [6]. In the studies reported here, the surface coverage was sufficiently low that the recombination kinetics of only the monohydride phase were studied.

The surface coverage of hydrogen during isothermal desorption was monitored as a function of time via laser-induced thermal desorption (LITD) measurements [7,8]. Briefly, the 308 nm output of a XeCl excimer laser (~ 2.0 mJ and $\theta_1 = 75^\circ$ with respect to the surface normal) serves to heat rapidly a 2.5 mm^2 elliptical spot on the $20 \times 20 \text{ mm}$ Si(100) surface and desorb the hydrogen from that spot. The desorbed molecular hydrogen is detected with an apertured (17.5 mm diameter) and differentially pumped quadrupole mass spectrometer. Care was taken to insure that the mass spectrometric signal from a laser shot scaled linearly with the surface coverage. By holding the surface temperature constant and using the laser to desorb the hydrogen from a series of spots, the change in the hydrogen coverage with time could be monitored. No damage of the surface attributable to the 2.0 mJ irradiation has been observed in over six months of repeated studies. Additional experimental details will be reported elsewhere [9].

The apparatus used in these experiments is a standard stainless steel bell jar 30 cm in diameter with a base pressure below 2×10^{-10} Torr. Surface order and cleanliness were confirmed by low-energy electron diffraction and Auger electron spectroscopy, respectively. A tungsten filament, 3 cm from the silicon surface and heated to 1640 K, was used to dissociate molecular hydrogen ($P_{H_2} = 10^{-6}$ Torr) during

adsorption. Thermal desorption mass spectrometry was used to calibrate the coverage as a function of exposure. The desorption peak maxima were at 783 K for the monohydride and 675 K for the dihydride with a heating rate of 2.3 K/s. In the isothermal desorption measurements reported here, the surface at 130 K was exposed to either atomic hydrogen or deuterium until the desired initial coverage was obtained. The surface was then heated (18.3 K/s) to the desired temperature (constant to \pm 0.2 K), and the LITD measurements were made as a function of time. Initial coverages of 1.0, 0.34 and 0.06 of the saturated monohydride were studied. The LITD signals were normalized to that of the saturated monohydride coverage.

The decrease in the fractional coverage of chemisorbed deuterium is shown as a function of time, parametric in temperature, in Fig. 1, for an initial coverage of 0.34 of the saturated monohydride. Similar data were recorded for both hydrogen and deuterium at nine different surface temperatures between 685 and 740 K. The data were quite reproducible from experiment to experiment at the same surface temperature, and for different initial surface coverages.

If the desorption reaction were second order, as commonly assumed, then the time derivative of the fractional surface coverage of hydrogen would be given by $d\theta_H/dt = -k_d\theta_H^2$, and a plot of $\frac{1}{\theta_H(t)}$ as a function of time would be linear. Here, k_d is the rate coefficient of desorption of hydrogen, which has the form $k_d = v_d(2)\exp(-E_d/k_B T)$. On the other hand, if the desorption reaction were first order, then $\frac{d\theta_H}{dt} = -k_d\theta_H$, and a plot of $\ln \theta_H(t)$ as a function of time would be linear. The data were analyzed in this fashion and a typical result, D₂ desorption at 735 K, is shown in Fig. 2. Data for each surface temperature and initial

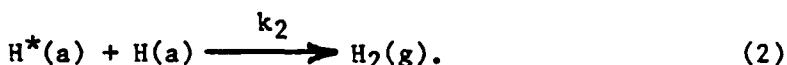
coverage, and for both D₂ and H₂ showed similarly good agreement with first-order kinetics and similarly bad agreement with second-order kinetics.

This demonstrates unequivocally that hydrogen desorption from the monohydride phase on Si(100) is first order. All traditional notions concerning adatom "hopping" on a surface, followed by recombination and desorption, are not appropriate, because this gives rise to second-order desorption kinetics. There is a completely different mechanism for desorption from this covalent surface compared to desorption from metals. Recent isothermal measurements of hydrogen desorption from Si(111), similar to those shown in Fig. 1, have been interpreted in terms of second-order desorption kinetics [8]. In those experiments, however, the fractional surface coverage of hydrogen was always greater than 0.2, which corresponds to times shorter than 300 s in Fig. 2. An analysis for this limited range of coverage is incapable of distinguishing between first- and second-order kinetics, and the desorption reaction is likely to be first order from Si(111) as well. The fractional coverage range displayed in Fig. 2 is $0.015 < \theta_D < 1$, and this wide range is necessary and sufficient for a meaningful analysis of the data. The fact that the desorption reaction is first order on both surfaces of silicon is suggested by the peak shape and the lack of a downshift in desorption peak temperature with increasing coverage in previous thermal desorption spectra [8,10-12], but most previous analyses have incorrectly assumed a second-order reaction.

The slope of the straight line in Fig. 2 is the rate coefficient for desorption of D₂ at 735 K. Similar rate coefficients were obtained at each temperature for both H₂ and D₂ desorption, and a plot of $\ln k_d$

as a function of reciprocal temperature is shown in Fig. 3. Based on Fig. 3, the apparent activation energies of H₂ and D₂ are each 47 ± 1 kcal/mol, and the preexponential factors of the desorption rate coefficients of H₂ and D₂ are $7.9 \times 10^{11} \text{ s}^{-1}$ and $5.6 \times 10^{11} \text{ s}^{-1}$, respectively. The ratio of the rates shows a normal kinetic isotopic effect, i.e. $k_d(H)/k_d(D) \sim 1.4$. It is also important to note that the fact that all constructions such as that shown in Fig. 2 are linear over the entire range of fractional surface coverages ($0.015 < \theta_{H(D)} < 1$) implies that the rate coefficients of desorption of H₂ and D₂ are not a function of surface coverage [13].

It is necessary to explain the desorption reaction in terms of a mechanism that is consistent with the observation of first-order kinetics and an apparent activation energy of approximately 47 kcal/mol. The challenge associated with the first issue is self-evident. The challenge associated with the second issue concerns the fact that in the usual analysis the activation energy must be larger than twice the Si-H bond energy [D(Si-H)] minus the H-H bond energy. The measured value of E_d then requires D(Si-H) to be less than 76 kcal/mol. However, values of D(Si-H) in various silane molecules are all much greater: a value of approximately 90 kcal/mol for this bond energy would be expected [14]. The following mechanistic model resolves both of these difficulties in a straightforward and physically appealing way. Hydrogen adatoms that are chemisorbed in their ground state on Si(100) are thermally excited irreversibly into a two-dimensional, delocalized band state. This excited, delocalized adatom (H^{*}) then reacts with a localized hydrogen adatom to produce H₂, which desorbs, i.e.



The concentration of H^* is always small if the first step is rate limiting, and this implies immediately that $\theta_{H^*} \approx k_1/k_2$, and that the rate of hydrogen desorption is given by $R_d = k_1 \theta_H$. The reverse of Eq. (1), quenching of H^* to produce a localized Si-H bond, is slow due to momentum conservation constraints analogous to those that are effective in "selective adsorption" scattering [16]. This mechanism explains the fact that the desorption reaction is first order, and the meaning of the low activation energy of the desorption reaction. The activation energy of 47 kcal/mol for the irreversible excitation to H^* reflects the extreme corrugation of the H-Si(100) potential in the plane of the surface, cf., the inset to Fig. 4. This should be expected for surfaces of covalent solids with directed dangling bonds. Note that if $D(Si-H) \sim 90$ kcal/mol, this implies that the H^* is bound (perpendicular) to the surface by approximately 43 kcal/mol. The delocalized H^* state is located further from the plane of the silicon surface than the localized Si-H species, and therefore the effective lateral corrugation that H^* experiences is weak.

The fact that the proposed mechanism is plausible and consistent with all experimental observations is insufficient, however, to verify its validity. We have demonstrated the validity of this mechanism unequivocally in the following way. Atomic hydrogen was exposed to a surface containing various subsaturation coverages of deuterium in the monohydride phase. The deuterium was adsorbed at 120 K, whereas the

hydrogen was exposed to the surface at 680 K for 100 s. In all cases, the deuterium was observed to react with the hydrogen and desorb, even though 680 K is far too low for any significant desorption to occur from the ground state surface adatoms during this period of time. For example, if a surface, on which $\theta_D \approx 0.5$ in the monohydride phase is initially present, is exposed to atomic hydrogen at 680 K (an exposure which would almost saturate the monohydride phase if the surface temperature were 120 K), then 45% of the deuterium originally present on the surface is removed, and the total final fractional coverage of hydrogen and deuterium is less than 0.7. In the absence of adsorbing hydrogen, the deuterium coverage would have decreased by approximately 1% at this temperature for the same period of time. The explanation for this observation is simple, and it establishes the validity of the proposed mechanism of desorption.

If the H^* species exists in the mechanism for desorption, it will also be a precursor in the adsorption of hydrogen. However, at elevated surface temperatures, the reaction $H^* + D \rightarrow HD$ is observed (vide supra). Assuming that $D(Si-H) = 90$ kcal/mol requires the activation energy for this reaction to be greater than 28 kcal/mol and less than 47 kcal/mol, which implies that the activation energy for dissociative adsorption of H_2 is less than 19 kcal/mol. This picture is summarized in the potential energy diagram of Fig. 4. The qualitative importance of this diagram is not affected by adopting the reasonable, 90 kcal/mole, value for $D(Si-H)$. Relative to an H_2 molecule in the gas phase as the energy zero, two localized hydrogen adatoms on the silicon surface lie at -75 kcal/mol, one delocalized adatom and one localized adatom lie at -28 kcal/mol, and two delocalized adatoms lie at + 19 kcal/mol. The dotted

curve shows qualitatively the barrier which $H_2(g)$ must overcome in order to chemisorb dissociatively.

The "reactive adsorption" measurement also demonstrates that the reaction between two H^* species is not required. The $H^* + H^*$ reaction would be unlikely based solely on arguments concerning the expected concentration of the H^* species, but would lead to a rate law, $R_d = k_1 \theta_H / 2$, which is indistinguishable from that of $H^* + H(a)$. Hence, it was necessary to preclude its occurrence in order to establish unambiguously our proposed mechanism.

To summarize, a new mechanism for the desorption of molecular hydrogen from the monohydride phase on Si(100) has been proposed and verified. The observed first-order desorption kinetics are due to the irreversible excitation of a hydrogen adatom into a delocalized, two-dimensional band state on the surface with the desorption reaction occurring between this excited hydrogen adatom and a second, localized hydrogen adatom. Both the kinetics and the mechanism of hydrogen desorption from the monohydride phase on Si(100) are now understood. A similar mechanism would be expected for hydrogen desorption from other surfaces of silicon, and from surfaces of other covalent solids.

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13. This does not, however, preclude the possibility of a compensation effect, i.e. both $v_d^{(1)}$ and E_d are functions of surface coverage, but the individual variations are such that $k_d = v_d^{(1)} e^{-E_d/k_B T}$ remains constant.
14. Typical bond strengths in various silane molecules are the following: $D(H-SiH_3) = 90.3$ kcal/mol, $D(H-SiH_2CH_3) = 89.6$ kcal/mol, $D(H-Si_2H_5) = 86.3$ kcal/mol and $D(H-SiH_2C_6H_5) = 88.2$ kcal/mol [15]. Note that the fact Si-H bond strengths in silane radicals can be lower (as low as 64 kcal/mol for H-SiH₂ [15]) is entirely irrelevant. The desorption of hydrogen from the mono-hydride phase on Si(100) involves no cleavage or formation of Si-Si bonds.
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Figure Captions

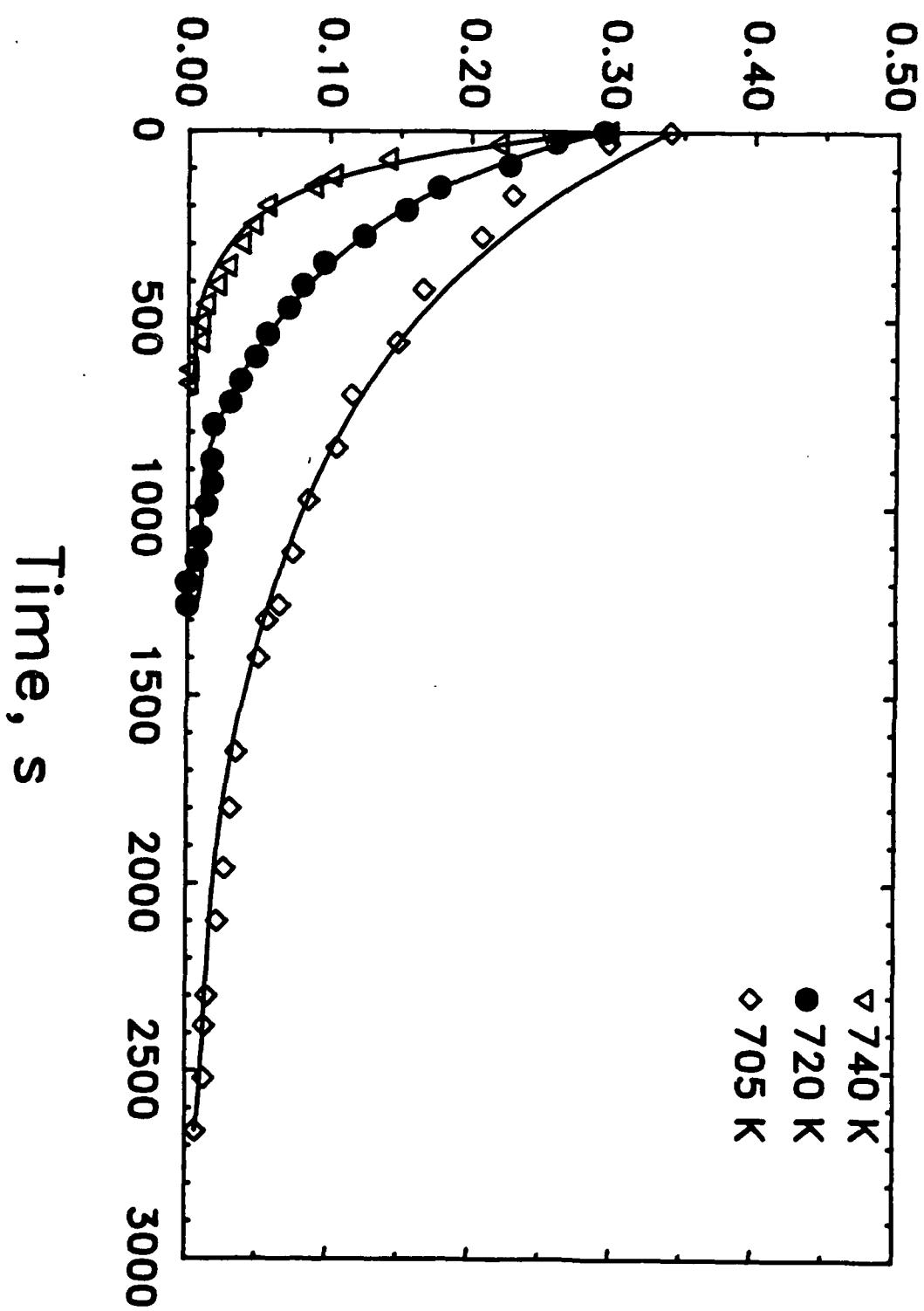
Figure 1: Variation in fractional surface coverage with time for the isothermal desorption of D₂ from Si(100).

Figure 2: A comparison of first-order and second-order kinetics of D₂ desorption from Si(100) at 735 K, demonstrating that the desorption reaction is first order.

Figure 3: Arrhenius plots for the desorption of H₂ and D₂ from Si(100). The implied activation energies and preexponential factors of the desorption rate coefficients are 47 ± 1 kcal/mol and 7.9 × 10¹¹ s⁻¹ for H₂, and 47 ± 1 kcal/mol and 5.6 × 10¹¹ s⁻¹ for D₂.

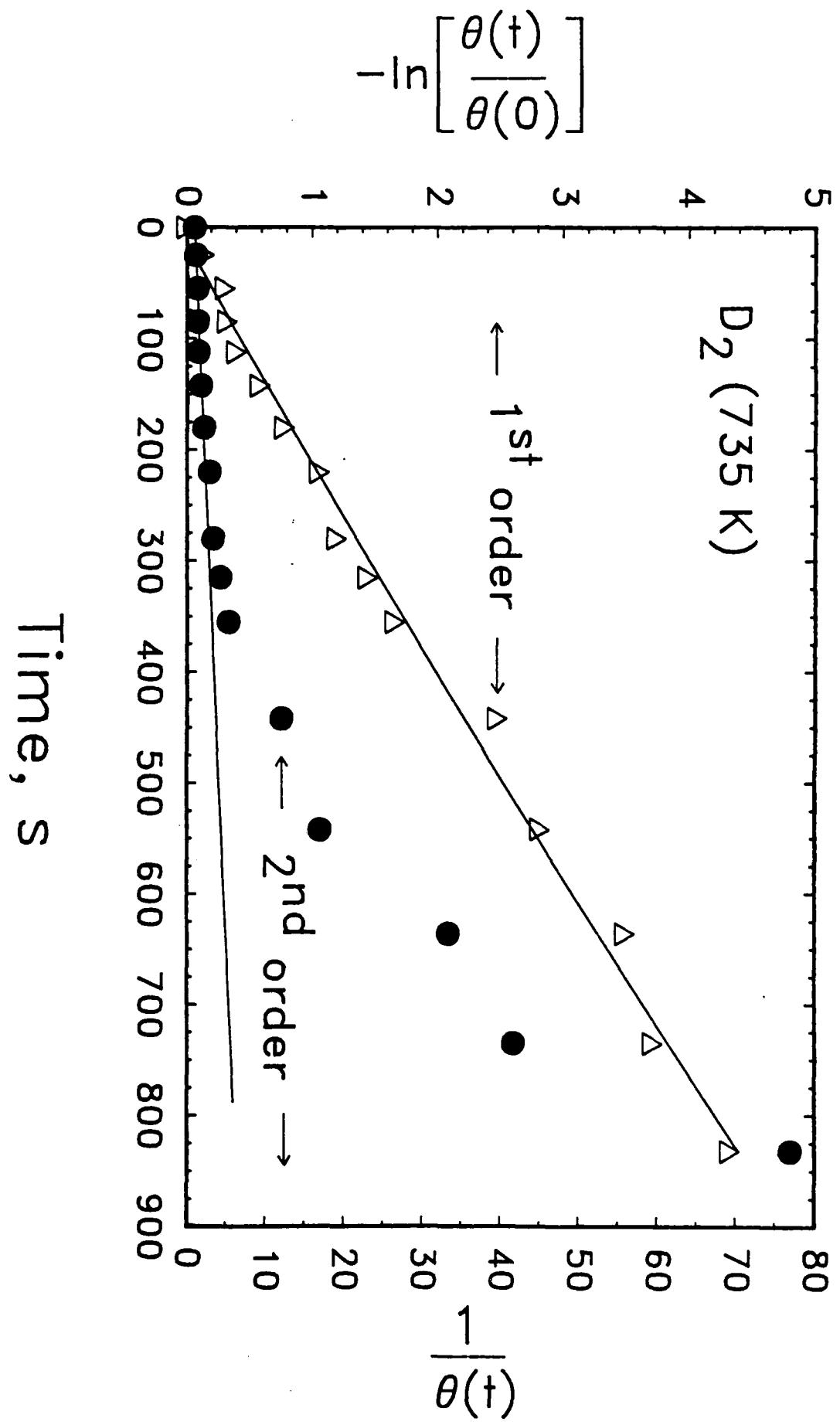
Figure 4: Potential energy diagram for the interaction of hydrogen with the Si(100) surface. The corrugation in the potential parallel to the surface is shown in the inset.

Deuterium Coverage



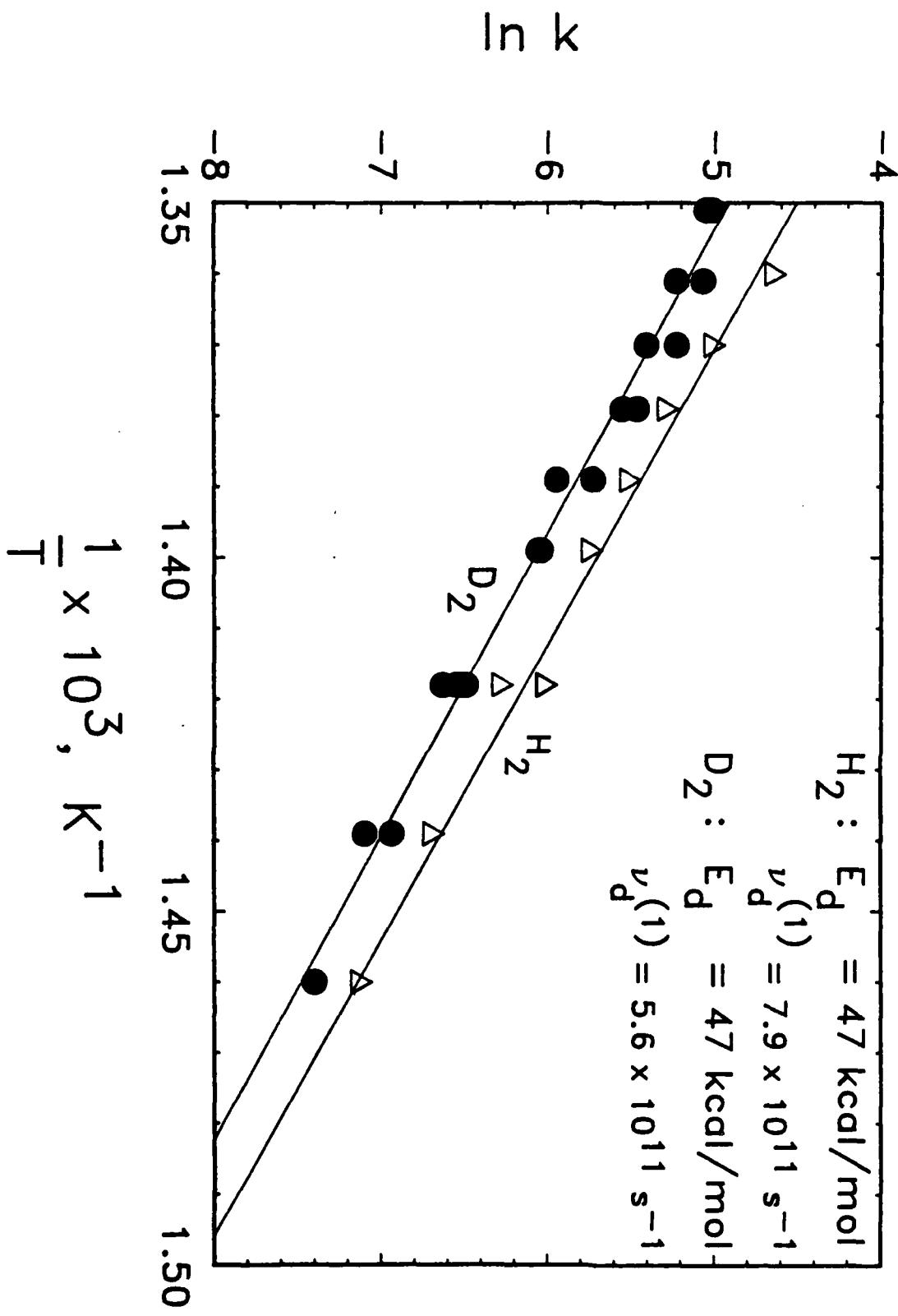
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Figure 1



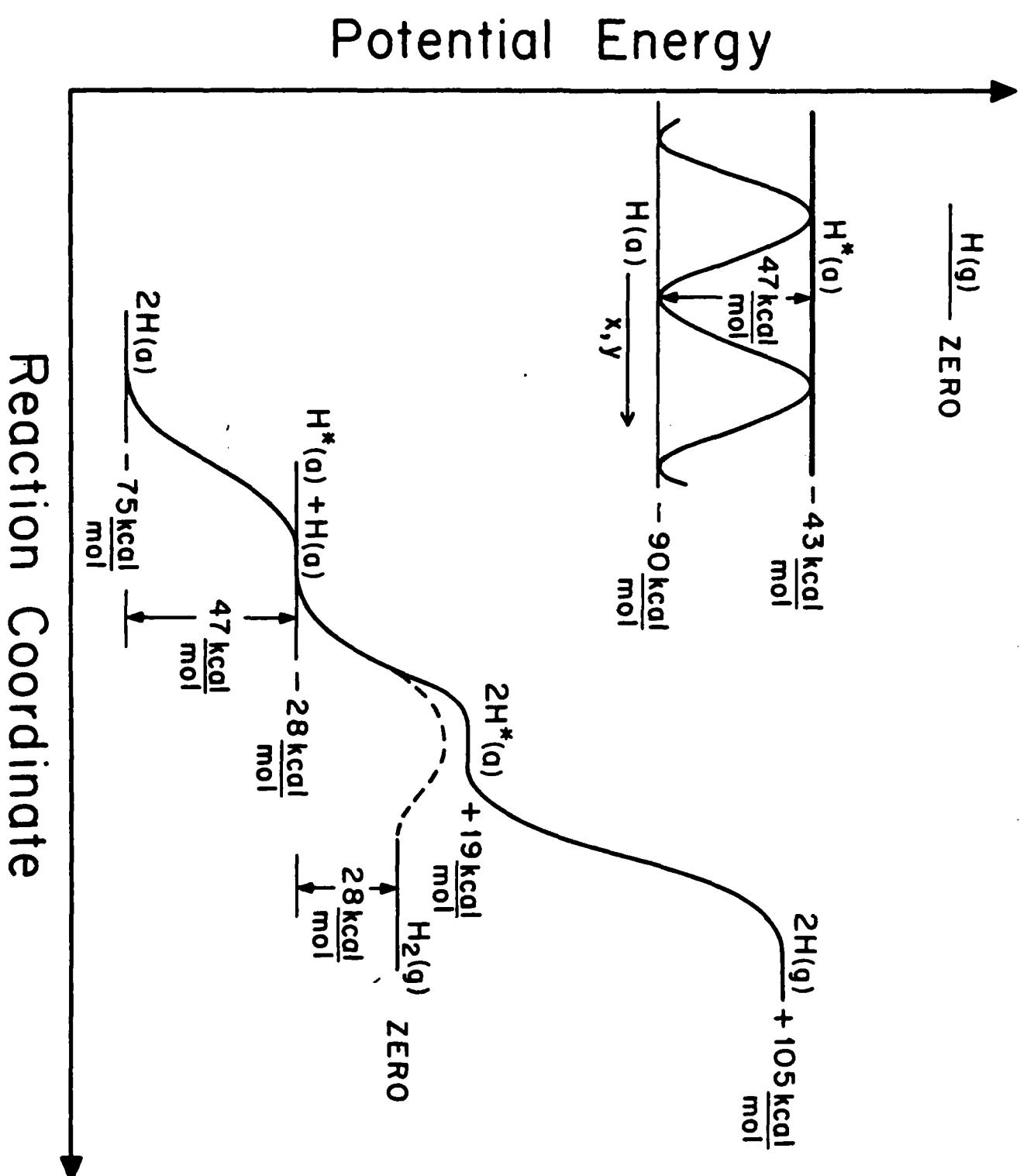
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Figure 2



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Figure 4

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